

Oxygen consumption upon electrochemically polarised zinc

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Abstract A Pt microelectrode was used to measure the oxygen consumption by redox reduction (ORR) on electrochemically polarised zinc in the redox competition mode. Zinc was polarised in the active and passive state, using a pH 7 and pH 13 solution, respectively. At pH 7, the oxygen concentration measured at a distance of 50 μm from the zinc surface, using the Pt microelectrode, is 15–60 % of the bulk oxygen concentration. Therefore, correspondingly, the oxygen consumption by zinc (due to ORR) is 40–85 % of the bulk oxygen concentration. At pH 13, where zinc undergoes passivation, the oxygen consumption by zinc is 70–80 % of the bulk oxygen concentration. The ORR rate on the surface of zinc passive films ($\text{ZnO}/\text{Zn}(\text{OH})_2$) is thus significant when compared to that on bare/actively corroding zinc. The influence of the electrode kinetics of zinc corrosion, on oxygen diffusion

towards the metal surface has been investigated in this study.

Keywords Zinc · Oxygen reduction reaction · Passivity · SECM · Oxygen

1 Introduction

In aqueous media, oxygen diffuses towards the metal surface before undergoing the oxygen reduction reaction (ORR) on its surface. The kinetics of ORR on zinc is usually estimated based on data accumulated during cathodic polarisation of the metal [1–3]. The current work focuses on measuring the extent of ORR on zinc during anodic polarisation in the active and passive state. ORR occurs as a two electron transfer reaction, during both cathodic and anodic polarisation of zinc, in conditions where an oxide layer is stable on its surface [2–8]. It was recently observed [8] that on potentiostatic anodic polarisation of zinc in an electrolyte of a passivating pH, there was a polarity reversal of passive currents from anodic to cathodic values. This suggests that ORR may take place at significant rates on the passive film, as it grows upon zinc. ORR on the passive film may facilitate the growth of zinc oxides, with ORR taking place at the oxide/solution interface and the complementary anodic reaction taking place on the metal surface [9–11]. The metal ions ejected into solution may precipitate as zinc oxides/hydroxides resulting in the overall growth of the zinc patina [8, 12–14]. It is necessary to determine the rate of ORR on passive films formed on zinc to clarify this aspect, and the current work emphasises on determining the oxygen consumption on zinc (by ORR) in the active and passive state. Oxygen diffusion through the electrolyte is known to be the rate-

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determining step for ORR on the surface of many reactive metals like Fe, Zn and Al [2, 3, 15–23]. In the current work, the impact of the electrochemical processes on oxygen diffusion towards the metal is investigated by measuring the local concentration of oxygen in solution.

1.1 Oxygen reduction reaction on zinc

1.1.1 Zinc in the active state

In non-passivating solutions, zinc corrodes in the active state, wherein a stable/protective passive film does not form on its surface [24]. Under these conditions, the Butler–Volmer equation prescribes that if zinc is anodically polarised with respect to the open circuit potential (OCP), the currents corresponding to metal dissolution (anodic currents) would increase exponentially, whereas simultaneously the cathodic currents would decrease exponentially [1]. Wagner and Traud's classic work [25] observed that the rates of the different Faradaic reactions on a surface are independent of each other, and are mainly a function of the electrode potential. Interestingly, several workers have found dependencies between anodic and cathodic reactions on the surface of different reactive metals like Cu, Al, Mg, etc. [26–30]. In the case of Mg, hydrogen evolution on its surface was found to increase during anodic polarisation, appearing to deviate from the mixed potential theory [30]. Since ORR is the main cathodic reaction which takes place on zinc, the oxygen consumption by ORR on the zinc surface needs to be measured, in order to estimate the extent of cathodic reactions on the metal surface during anodic polarisation.

1.1.2 Zinc in the passive state

When zinc is polarised in passivating solutions, a passive film usually forms on the zinc surface [12]. This results in approximately steady currents being manifested during potentiostatic anodic polarisation. The current–voltage relation in this case does not follow the exponential relation prescribed by the Butler–Volmer equation [13]. During potentiodynamic polarisation of zinc in neutral solutions, ZnO has been electrochemically detected on the surface during cathodic polarisation [18]. It is observed that ORR changes from a four electron mechanism to a two electron mechanism once the passive oxide forms upon zinc [2–8, 18]. The existing body of work on zinc passivation does not qualitatively or quantitatively reveal the rate of ORR on zinc/zinc oxides as it undergoes passivation (at potentials anodic to the OCP). ORR on the passive films may impact the local electrochemistry of the system [11] and the products released by the different steps of the ORR may influence the kinetics of passivation [4]. In the case the

passive films are porous, ORR can take place on the oxide surface or the metal surface [11]. The kinetics of ORR on the oxide surface relative to that on the metal surface will dictate the extent of ORR on the oxide and the overall corrosion rate of the metal [11]. It is, therefore, essential to have a measure of ORR on passive films formed on zinc, and its comparison with ORR on bare/actively corroding zinc.

1.2 Measuring oxygen consumption on zinc using a Pt microelectrode

Oxygen concentration measurements on the surface of metals have been carried out in the context of scanning electrochemical microscopy (SECM) [31–37]. Here, a Pt tip is held at specific potentials where it undergoes the ORR to measure the local oxygen concentration [32]. In these experiments, the SECM is operated in the redox competition mode (RC-SECM) mode [32]. In this mode, the Pt tip and the sample (zinc) compete for reactions with same analyte in the solution. Oxygen reduction at the Pt tip will lead to a constant current signal unless the tip is positioned above a competing O₂ consuming site, which will locally alter the O₂ concentration concomitantly leading up to a diminished current flow through the Pt tip [32].

2 Experimental

During each experiment, two electrochemical systems are operated simultaneously. One system involves the zinc substrate which is polarised to different potentials with the corresponding electrode currents being measured (chronoamperometry). The other involves the Pt microelectrode which is positioned over the zinc substrate and is also simultaneously polarised to different potentials to measure the currents corresponding to ORR on its surface. The electrochemical systems were electrically isolated from each other using an isolation transformer, which was used to supply power to one of the two potentiostats. The Pt microelectrode thus serves to sense the oxygen consumption upon zinc. The experimental details for these specific systems are listed separately.

2.1 Material and electrolytes

Samples used in this work were Zintane Z83 (99.96 % zinc) alloy (Union Minière, France) [38, 39]. Samples with a surface area of 2 by 2 mm² were mounted in epoxy resin, forming the substrate. An electrochemical cell was designed to enclose this substrate and also hold both the counter electrode (platinised Ti mesh counter electrode)

and the reference electrode (saturated calomel electrode) at fixed positions. Sufficient leeway is provided within the electrochemical cell to be able to move a Pt tip to different locations without any restriction. The zinc substrate was successively ground to 2,000 grit SiC paper prior to the experiments. The zinc substrate was polarised to different potentials using a potentiostat (CH Instruments, TX, USA). The chronoamperometric currents and electrode potentials were also recorded using this instrument. Zinc is exposed to a different variety of solutions in these experiments namely distilled water (with dilute NaOH added to achieve neutral pH), 0.001 M sodium carbonate solution, 0.0001 M ammonium tartrate solution (buffered to pH 7) and an unbuffered pH 13 (0.1 M NaOH) solution. The pH 7 solution serves to study zinc corrosion in the active state, whereas the pH 13 solution could be used to study zinc in both the active and passive state [38]. Estimating the extent of ORR taking place on zinc, in a pH 7 and pH 13 solutions will enable a qualitative comparison of the extent to which a passive zinc surface supports the ORR with respect to bare/actively corroding zinc.

2.2 Oxygen current measurements and the Pt microelectrode

Platinum microelectrodes (manufactured by CH, Instruments, TX, USA) were used in the experiments, having a diameter of 10 μm . The quality of the Pt microelectrode was regularly assessed by performing cyclic voltammetry in 0.5 mM Ferrocenemethanol solution (for the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox reaction). These microelectrodes were also regularly cleaned and polished using a polishing pad with aluminium carbide slurry (with 0.3–1- μm -sized particles). The SECM measurements were carried out with the Scanning Electrochemical Workstation Model 370 (Princeton Applied Research, AMETEK Inc). The diffusion regime for the ORR on a Pt microelectrode is between -0.6 and $-0.8 V_{\text{SCE}}$ [35, 36]. Therefore, by holding the Pt tip at a potential in this range, the oxygen concentration could be sensed in the local environment. In one study, within this work, the Pt tip is held at $-0.7 V_{\text{SCE}}$ and positioned at different heights ranging from 50 to 1,000 μm over the zinc sample, to measure the oxygen concentration at each height. Zinc is thus exposed to different solutions (distilled water, carbonate solution, NaOH solution with pH 13) in which it corrodes at different rates, and the corresponding oxygen currents at different heights are measured.

2.3 In situ oxygen production and measurement

An in situ oxygen production/measurement approach is used in the current work for the oxygen current

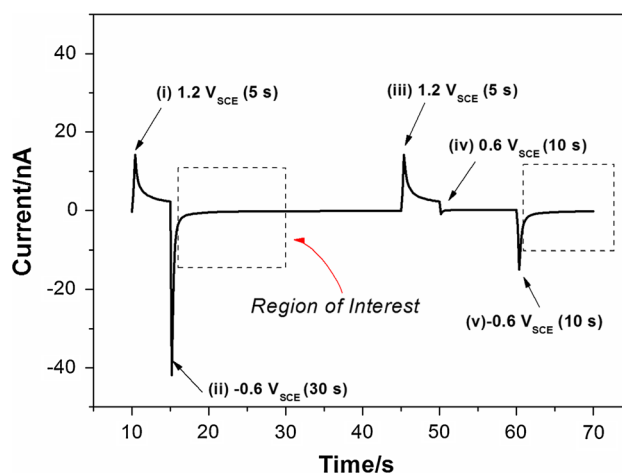


Fig. 1 Steps (i–v) illustrated on a current–time plot performed on the Pt microelectrode. The oxygen currents to assess the consumption of oxygen by zinc are captured from the regions boxed

measurements, adapted from [32]. Here, the Pt tip is used to produce oxygen by holding it at a certain potential, the oxygen produced is then immediately consumed by both Pt and zinc. Since both the metal surfaces compete for oxygen, the oxygen currents recorded on Pt give an appraisal of the oxygen consumption on zinc. The microelectrode is positioned at 50 μm above the zinc substrate, since oxygen diffuses at a rate of about 10 μm in 0.1 s [40], making it necessary to have the tip as close as possible to the substrate. The following are the steps in the experiments involving the Pt electrode (Fig. 1); initially prior to the experiment, the Pt microelectrode is polarised to $-0.6 V_{\text{SCE}}$ for 10 s, under these conditions both Pt and Zn consume oxygen under diffusion control. The Pt microelectrode is then

- (i) Polarised to $1.2 V_{\text{SCE}}$ for 5 s, here water is electrolysed and oxygen is evolved on the Pt electrode.
- (ii) Polarised to $-0.6 V_{\text{SCE}}$ for 30 s, wherein the oxygen evolved from (i) is immediately consumed by both the Pt tip and zinc (under diffusion control). The variation in currents measured on the Pt tip could thus be used to estimate the consumption of oxygen by the zinc substrate (by ORR).
- (iii) Polarised to $1.2 V_{\text{SCE}}$ for 5 s again.
- (iv) Polarised to $0.6 V_{\text{SCE}}$ for 10 s, here ORR is favoured as a two electron process on the Pt tip.
- (v) Polarised to $-0.6 V_{\text{SCE}}$ for 10 s, wherein the oxygen evolved from (iii) is immediately consumed by both the Pt tip and zinc (under diffusion control). This test serves as a replicate

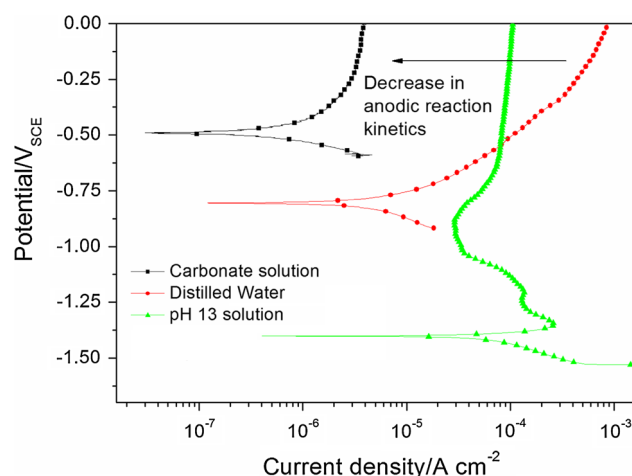


Fig. 2 Potentiodynamic polarisation curves of zinc exposed to 3 different solutions: (i) 0.001 M sodium carbonate (ii) distilled water and (iii) 0.1 M NaOH solution (pH 13). Zinc exposed to the carbonate solution has the slowest anodic reaction kinetics

for (i–ii). The currents detected in step (iv) are not presented/analysed in the context of the current work, and only the currents measured during (ii) and (v) corresponding to the oxygen consumption are presented/analysed (indicated by boxed areas in Fig. 1).

The currents measured for the first 2–3 s of steps (ii) and (v) are not considered for analysis, as the electrode is recovering from the preceding voltage spike. Prior to each experiment where zinc is polarised, the Pt microelectrode is first positioned at 1,000 μm above the zinc surface and steps (i–v) are carried out. The currents measured in this case approximately correspond to the bulk oxygen concentration, and hence serve to normalise all following measurements. The counter electrode is placed several centimetres from the zinc substrate/Pt tip to avoid any interference with the oxygen consumption on both zinc and Pt. All experiments were carried out multiple times to ensure reproducibility of the results, prior to undertaking data analysis. The bipotentiostatic mode of electrochemical testing, wherein a substrate and the microelectrode are simultaneously polarised, has been undertaken by several researchers for different systems [37, 40]. The approach used herein serves to obtain a qualitative comparison between the extent of ORR on active and passive zinc surfaces, during anodic polarisation. In conventional electrochemical tests (like potentiodynamic polarisation), it is difficult to ascertain the kinetics of a cathodic process during anodic polarisation, either quantitatively or qualitatively.

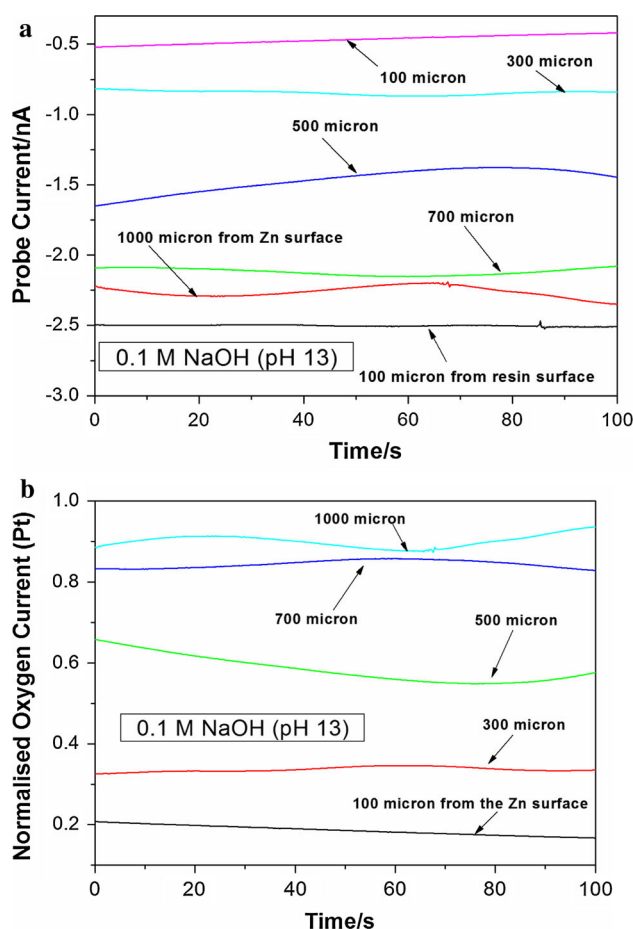


Fig. 3 a Oxygen currents (on Pt microelectrode) measured upon a zinc sample embedded in an insulating resin, the current measurements were carried out at different heights. The oxygen currents (Pt) measured at a height of 100 μm from the resin are close to that recorded at a height of 1,000 μm upon zinc, displaying the sensitivity of the Pt tip in recording oxygen consumption on zinc. **b** Normalised oxygen current (Pt) at different heights upon zinc in a pH 13 solution. The oxygen current corresponding to the resin surface (Fig. 3a) is taken as 1

3 Results

3.1 Zinc electrode kinetics and the effect on oxygen diffusion

The potentiodynamic polarisation curves of zinc in distilled water (close to neutral pH), 0.001 sodium carbonate and 0.1 M NaOH (pH 13) solutions are shown in Fig. 2. The potentiodynamic polarisation was carried out from -150 mV versus the open circuit potential to $0.0\text{ V}_{\text{SCE}}$. The scan rate used was 1 mV/s . It can be seen that the corrosion rates of zinc in all the three solutions are different, the highest being in the pH 13 solution followed by that in distilled water and the carbonate solution. The anodic branches of the polarisation curves significantly

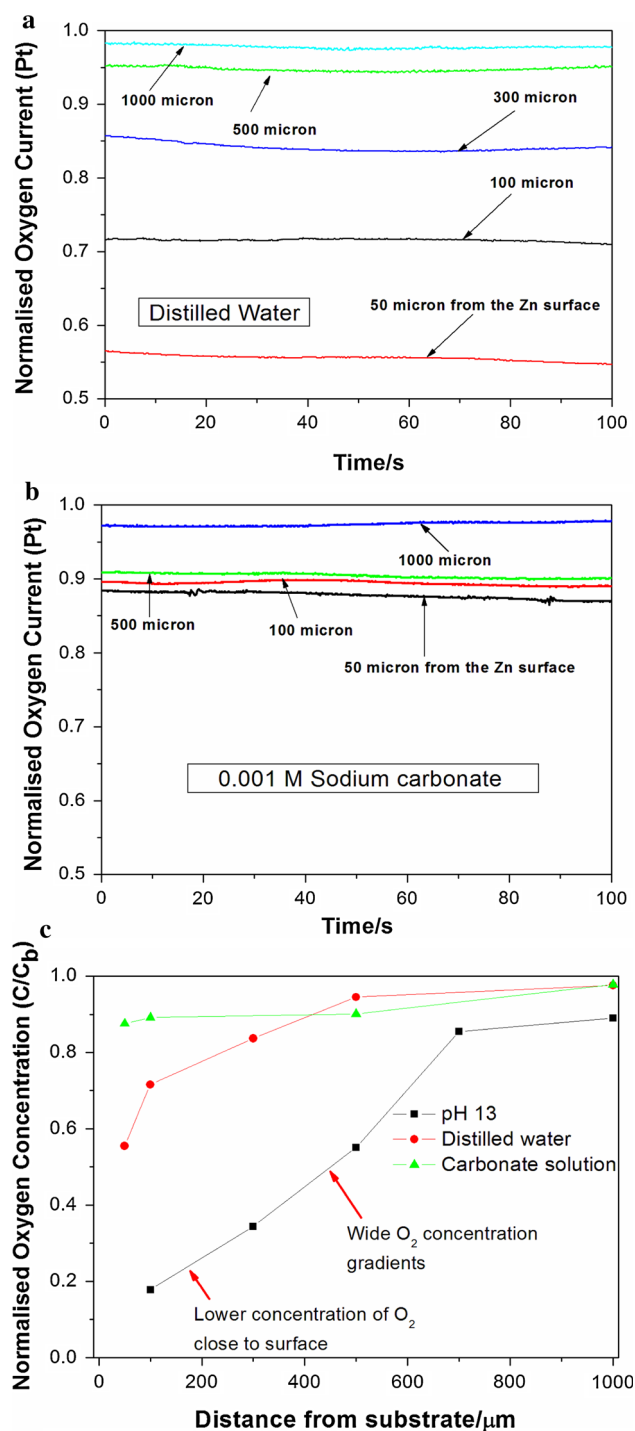


Fig. 4 **a** Normalised oxygen currents (Pt) at different heights over zinc in distilled water. **b** Normalised oxygen currents (Pt) at different heights over zinc in a 0.001 M sodium carbonate solution. **c** Comparison between the normalised oxygen currents of zinc exposed to the three solutions at a particular instant

shift towards the left in case of the carbonate solution suggesting that there is an inhibition of the zinc dissolution reaction in this case, and, therefore, under open circuit conditions, the electrode kinetics of zinc dissolution in the

carbonate solution is much slower than that in distilled water and the pH 13 solution.

The oxygen currents measured using a Pt microelectrode in a redox competition mode when positioned at different heights (100–1,000 μm) over zinc in a pH 13 solution are shown in Fig. 3a. The oxygen currents have been normalised with respect to the currents measured when the Pt tip is positioned over the resin (at a height of 100 μm). At a fixed position of 100 μm over the resin surface, the oxygen currents measured using the Pt tip are very close in magnitude to those measured at 1,000 μm over the zinc sample. Whereas at 100 μm over zinc, the oxygen currents are only 20–30 % of those measured over the resin surface (at the same height). This implies that a large quantity of oxygen is being consumed by the zinc surface, and the Pt tip is capable of sensing these variations. From Fig. 3b, it is evident that the oxygen currents vary considerably within the pH 13 solution, when in contact with zinc. There is significant oxygen depletion at least up to 1,000 μm above the zinc surface. It is, therefore, clear that oxygen is consumed at extremely high rates on the zinc surface causing large concentration gradients (given by the ratio of the difference in oxygen currents/concentrations at two heights to distance between the two heights) in solution.

In distilled water (pH close to 7), the oxygen consumption at 100 μm from the zinc surface is 70 % of the bulk (Fig. 4a), and it is also observed that the oxygen concentration gradients for oxygen are smaller than at pH 13. In the carbonate solution with the lowest corrosion rate, it is seen in Fig. 4b that the oxygen currents measured at a distance of 100 μm above zinc are 80–90 % of those measured in the bulk solution. There are oxygen concentration gradients in distilled water and the carbonate solution too, however, they are not as large as those in the pH 13 solution. A comparison of the normalised oxygen currents in the three solutions is shown in Fig. 4c. When zinc is exposed to the carbonate solution (with slow anode reaction kinetics), a lower quantity of oxygen is consumed on its surface, and also the concentration gradients are smaller when compared to that in the pH 13 solution. Slower anode reaction kinetics on the metal surface (at OCP), thus, results in lower oxygen consumption on its surface and smaller oxygen concentration gradients in solution. The diffusion rate of oxygen is directly proportional to the oxygen concentration gradient implying that the slower the kinetics of zinc dissolution at OCP, the slower the rate of oxygen diffusion towards the metal.

3.2 Zinc in the active state

The OCP variation of zinc in a 0.0001 M Ammonium tartrate solution buffered to pH 7 is shown in Fig. 5a. The OCPs of zinc are in the range from -0.96 to -0.98 V_{SCE} in

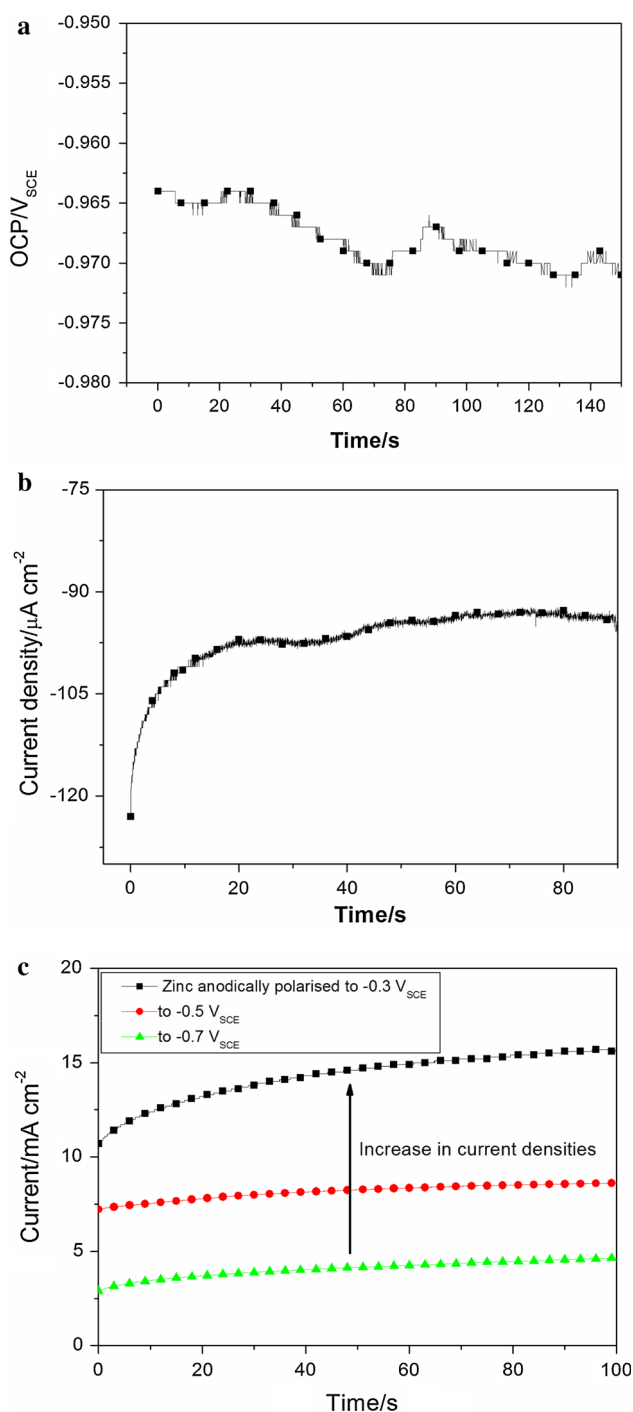


Fig. 5 **a** OCP of zinc in 0.0001 M ammonium tartrate solution buffered to pH 7. **b** Potentiostatic currents measured on zinc cathodically polarised to $-1.1 V_{SCE}$. **c** Potentiostatic currents measured on zinc anodically polarised to different potentials, -0.7 , -0.5 and $-0.3 V_{SCE}$

this solution. The potentiostatic currents when zinc is cathodically polarised to $-1.1 V_{SCE}$ are shown in Fig. 5b. Similarly, the potentiostatic currents when zinc is anodically polarised to the different anodic potentials of -0.7 ,

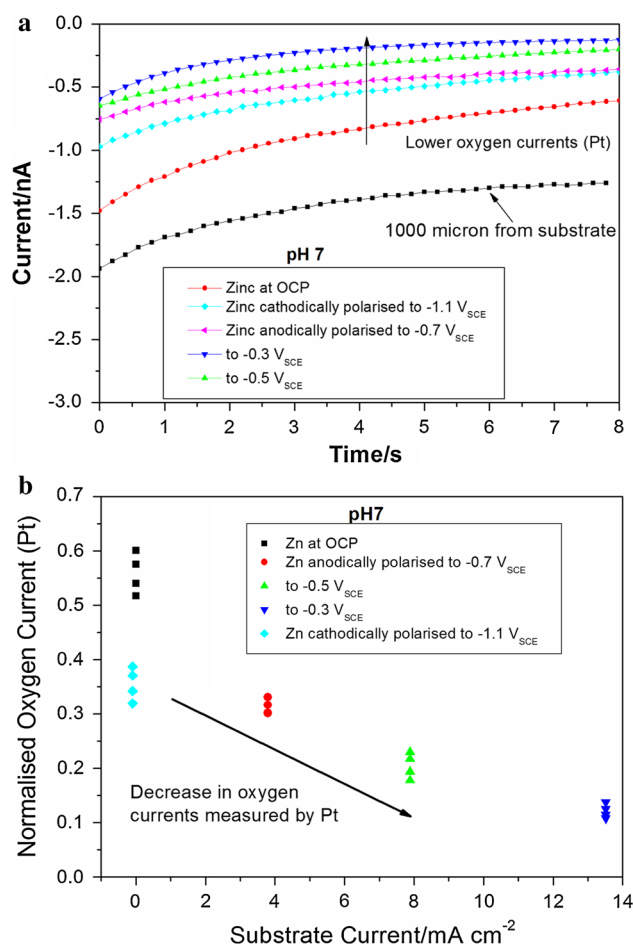


Fig. 6 **a** Oxygen currents measured on the Pt tip when positioned at 50 μm above the zinc substrate subject to different potentials (Fig. 5b, c). **b** Normalised oxygen currents measured on zinc derived from **a**

-0.5 and $-0.3 V_{SCE}$ are shown in Fig. 5c. As expected with an increase in the anodic potential applied to zinc, the potentiostatic currents also increase.

The oxygen currents measured using the Pt tip located 50 μm above the zinc substrate in the pH 7 solution, when the zinc substrate is at OCP, and also polarised to the different potentials are shown in Fig. 6a. These currents are then normalised with respect to the oxygen currents measured at 1,000 μm from the zinc surface (it is an approximation for bulk concentration of oxygen). Figure 6b shows the normalised oxygen currents plotted against the potentiostatic currents recorded on zinc (Inferred from Figs. 5c and 6a). The normalised oxygen currents (Pt) measured when zinc is at OCP, at distance of 50 μm from the surface are in the range from 0.5 to 0.6. This implies that the quantity of oxygen detected by the Pt tip, at a 50- μm distance from zinc, is around 50–60 % of the bulk oxygen concentration (closely corresponding to the measurements in Figs. 6a). Therefore, correspondingly, the oxygen

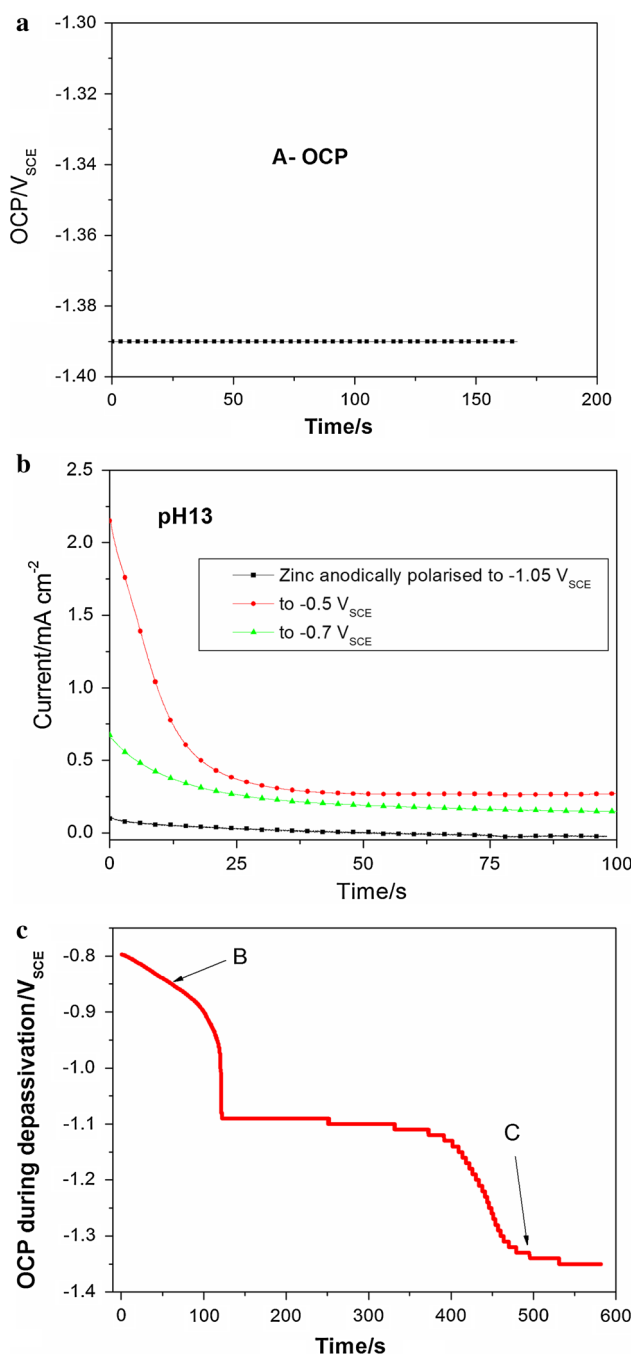


Fig. 7 **a** OCP of zinc in 0.1 M NaOH solution at pH 13. **b** Potentiostatic currents measured on zinc anodically polarised to -1.05 , -0.7 and -0.5 V_{SCE}. **c** OCP measurements during the depassivation of zinc. **b** and **c** represent points where oxygen current measurements were made using the Pt microelectrode

consumption by zinc (due to ORR) at a 50- μ m distance from the zinc surface is 40–50 % of the bulk oxygen concentration.

Higher oxygen currents detected by the Pt tip imply that more oxygen is available in the local environment for the Pt tip to consume, indicating that a lower quantity of

oxygen is being consumed on the zinc surface. Lower magnitude of oxygen currents (Pt) imply that more oxygen is consumed on zinc (by ORR) in the redox competition mode. As zinc is polarised to the anodic potentials, the oxygen currents measured on the Pt tip decrease (Fig. 6b). The normalised oxygen currents at OCP are around 0.5, but they progressively decrease to around 0.1 when zinc is polarised to -0.3 V_{SCE}, implying that with an increase in anodic potentials, zinc tends to consume more oxygen. During cathodic polarisation (at -1.1 V_{SCE}), the normalised oxygen currents (Pt) are in the range of 0.3–0.4, closer to that when zinc is at OCP (0.5–0.6).

3.3 Zinc in the passive state

In a pH 13 solution, the OCP of zinc typically settles in the range from -1.35 to -1.38 V_{SCE} [8, 38, 41] (Fig. 7a) as Zn is in a state of dynamic equilibrium with $\text{Zn}(\text{OH})_4^{2-}$ ions, which is the most thermodynamically stable zinc phase at this pH [8]. When zinc is anodically polarised to its passive regime at different potentials namely -1.05 V_{SCE}, -0.7 V_{SCE} and -0.5 V_{SCE} (Fig. 7b), passive oxides form upon zinc [41], but these oxides are still prone to dissolution, since the bulk pH is highly alkaline [8]. This results in high passive currents at this pH. During the potential hold at -1.05 V_{SCE}, the passive currents drop to extremely low values of the order of few tens of microamperes. At -0.7 V_{SCE} and -0.5 V_{SCE}, the passive currents are much higher than those at -1.05 V_{SCE}. After undergoing passivation, the OCP of zinc typically settles in the range from -0.7 to -0.8 V_{SCE} due to the formation of some stable passive oxides on its surface. Since the outer precipitated layer is unstable, the passive oxide has a tendency to dissolve into $\text{Zn}(\text{OH})_4^{2-}$ ions [8], causing the OCP to gradually drop back to the range from -1.35 to -1.38 V_{SCE} with time. Initially, there is a sharp drop from -0.8 V_{SCE} to around -1.1 V_{SCE}, implying that the protective passive oxides are undergoing dissolution (depassivation). The OCP then remains stable for a short span between -1.1 and -1.2 V_{SCE}, after which there is another sharp drop to around -1.35 V_{SCE} (Fig. 7c), suggesting that some other oxides are dissolving into the solution. Ultimately, zinc returns to the initial active state at this pH, in equilibrium with the $\text{Zn}(\text{OH})_4^{2-}$ ions.

The oxygen currents measured using the Pt tip, over zinc at OCP, and the three anodic potentials are displayed in Fig. 8a. The normalised oxygen currents are shown in Fig. 8b. During passivation, the oxygen currents (Pt) measured over zinc increase when compared to zinc is at OCP. When zinc is at OCP, the normalised oxygen currents (Pt) are around 0.15, whereas when zinc is anodically polarised, the normalised oxygen currents tend to increase and settle in the range of 0.2–0.3. This translates to a local oxygen concentration of 20–30 % of the bulk oxygen

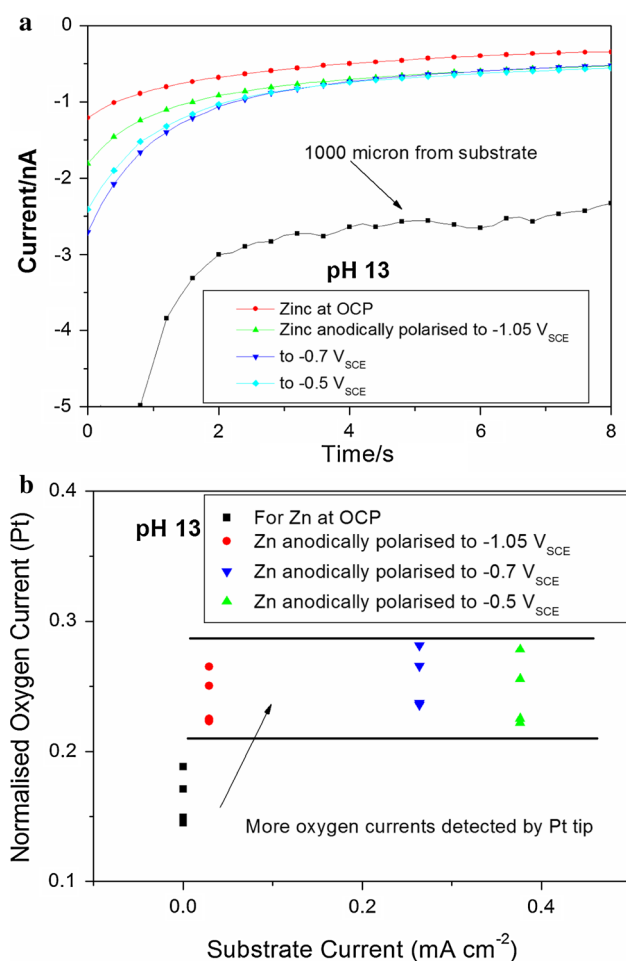


Fig. 8 **a** Oxygen currents measured on the Pt tip when positioned at $50 \mu\text{m}$ above the zinc substrate subject to different potentials (based on Fig. 7). **b** Normalised oxygen currents measured on zinc derived from **a**

concentration. Therefore, the oxygen consumption by zinc (due to ORR) polarised at these potentials, at a $50\text{-}\mu\text{m}$ distance from the zinc surface is 70–80 % of the bulk oxygen concentration. This implies that less oxygen is consumed by zinc as it undergoes passivation than when it is at OCP, and that overall zinc consumes a significant quantity of oxygen, by ORR, during passivation.

The oxygen currents measured at points B and C (refer Fig. 7c) and when zinc is at OCP (Fig. 7a) are shown in Fig. 9a. It shows that as zinc undergoes depassivation, a large quantity of oxygen is consumed on its surface. Figure 9b shows the normalised oxygen currents (Pt) plotted against the OCP of zinc during depassivation. The normalised oxygen currents (Pt) measured at points B and C are very close in magnitude to that when zinc is at OCP (A), suggesting that during depassivation, the oxygen consumption by ORR on zinc does not vary significantly.

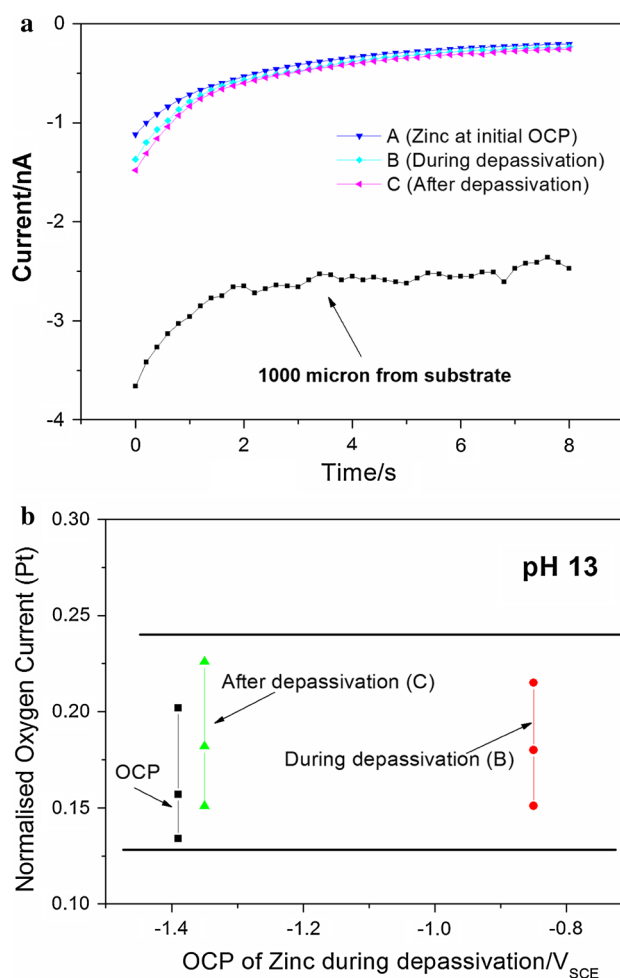


Fig. 9 **a** Oxygen currents measured on the Pt tip when positioned at $50 \mu\text{m}$ as zinc undergoes depassivation. The oxygen current measurements are done in the vicinity of points **b** and **c** in Fig. 7c. **b** Normalised oxygen currents (Pt) measured on zinc in a pH 13 solution, during depassivation, as a function of the zinc OCP

3.4 Comparison between oxygen consumption on zinc in the active and passive state

Wagner and Traud [25] proposed that the rate of a Faradaic reaction taking place on the surface of a metal is independent of other Faradaic reactions on the same surface. The rate of the electrochemical reaction mainly depends on the electrode potential, implying that the overpotential for a particular electrode reaction drives the rate of that reaction (current). The normalised oxygen currents (Pt) measured over zinc in both the active and passive state are plotted against the potentials of the zinc electrode in Fig. 10 (data inferred from Figs. 5, 6, 7). Thus, the oxygen consumption by ORR on zinc, as a function of the electrode potential (related to the overpotential for the ORR) can be inferred.

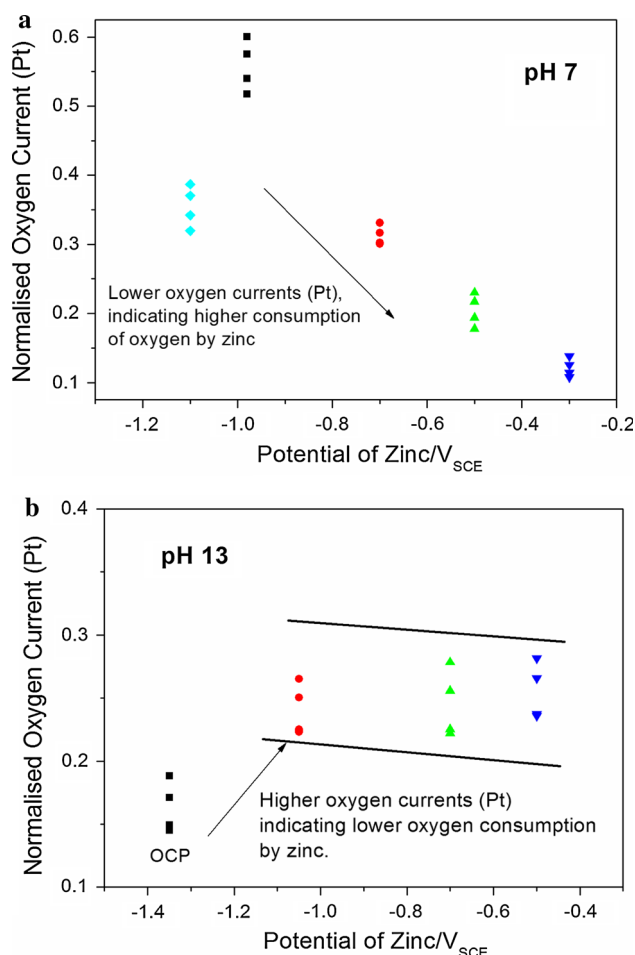


Fig. 10 **a** Normalised oxygen currents (Pt) measured on zinc in a pH 7 solution as a function of electrode potentials. **b** Normalised oxygen currents (Pt) measured on zinc in a pH 13 solution as a function of electrode potentials

At similar electrode potentials (in the range from $-1.05 V_{SCE}$ to $-0.5 V_{SCE}$), the anodic currents of zinc in a pH 7 solution (in the range of $2.5\text{--}10 \text{ mA/cm}^2$) are significantly higher than that of zinc in a pH 13 solution (in the range of $0.01\text{--}2 \text{ mA/cm}^2$) (refer Figs. 5c, 7b). This implies that zinc is covered by a passive layer in the pH 13 solution during anodic polarisation. The normalised oxygen current (Pt) measured close to zinc surface in pH 7 solution increases with the anodic potentials and is in the range (0.6–0.15). In a pH 13 solution, where zinc undergoes passivation, the normalised oxygen current (Pt) is in the range (0.2–0.3). Therefore, in a pH 13 solution during passivation, since the normalised oxygen currents (Pt) measured are low (and comparable with that of actively corroding zinc), the surface consumes a significant quantity of oxygen (predominantly by ORR). The passive oxides formed upon zinc, under these conditions thus support ORR at significant rates (compared to bare zinc) on their surface.

4 Discussion

4.1 The electrode kinetics of zinc dissolution and oxygen diffusion

Zinc is an active metal, with a high exchange current density for zinc dissolution [18, 19]. The kinetics of ORR on zinc is relatively slower when compared to that of metal dissolution; the ratio of the exchange current densities of metal dissolution to that of ORR on zinc is of the order of 10^9 when compared to Fe (around 10^2) [19]. In bulk solutions, thus, oxygen diffusion and ORR on zinc are the rate-limiting processes for zinc corrosion [2, 3]. It is evident from Figs. 2, 3, 4 (Sect. 3.1) that as the corrosion potential of zinc becomes less noble (faster kinetics of zinc dissolution), there is more oxygen consumed on its surface. The electrode kinetics of zinc dissolution, thus, determines the corrosion potential of zinc (Fig. 2), which in turn controls the oxygen diffusion/oxygen consumption patterns in zinc-based systems (Fig. 4c).

4.2 ORR on zinc

4.2.1 Zinc in the active state

Oxygen consumption on zinc increases during anodic polarisation from the OCP (Sect. 3.2). During cathodic polarisation, the metal is still below its standard oxidation potential (for zinc it is around $-1.1 V_{SCE}$ [24]), but the overpotential for ORR on the metal surface is higher than that at OCP. Oxygen consumption on zinc, under these conditions, predominantly takes place by the ORR on zinc. The overpotential for the ORR decreases during the anodic polarisation of zinc; however, it is observed that the oxygen consumption by zinc during anodic polarisation increases with applied potential (Refer Fig. 10a). This may be because of an increase in the surface area of the electrode during the high rate of metal dissolution experienced on anodic polarisation. There is also a possibility that zinc may consume oxygen by some unidentified non-electrochemical reactions, however, this cannot be determined from the current experimental results.

4.2.2 Zinc in the passive state

In a pH 13 solution, under open circuit conditions, the oxide film formed on zinc is not stable and rapidly dissolves into Zn(OH)_4^{2-} ions [8]. The corrosion potential of zinc drops to extremely cathodic values, making the overpotential for the ORR high which, therefore, may result in the ORR taking place at high rates on the zinc surface. When zinc is anodically polarised to $-1.05 V_{SCE}$, it undergoes passivation [8] and the potentiostatic current drops to a few 10 s of

microamperes (Fig. 7b). In this case, the oxygen consumption by the passive zinc surface is still high; the normalised current measured at a distance of 50 μm from the zinc surface is around 0.2–0.3. This implies that local oxygen concentration is only 20–30 % of the bulk oxygen concentration (Fig. 10b). It can be assumed that the oxygen consumption by zinc (due to ORR), at a distance of 50 μm , from the surface is thus 70–80 % of the bulk oxygen concentration. This is comparable with that on an actively corroding zinc surface at pH 7, where the oxygen consumption is 40–85 % of the bulk oxygen concentration (normalised oxygen current range of 0.15–0.6 Fig. 10a). At similar overpotentials for the ORR, if the two different surfaces (active and passive) consume oxygen by ORR at comparable rates, it implies that the kinetics of ORR on both the surfaces is comparable. Therefore, the rate of ORR on the surface of zinc passive films ($\text{ZnO}/\text{Zn}(\text{OH})_2$) is significant (equal or slightly higher) when compared to that on bare/actively corroding zinc.

A porous oxide model of corrosion proposed that the electrons released during the metal dissolution reaction may escape through the metal into the oxide and get consumed by the ORR, which takes place at the oxide/solution interface [11]. The current work shows that during passivation, ORR takes place at significant rates on the oxide surface (compared to actively corroding zinc). This suggests that as zinc dissolves in the passive state, electrons may be ejected into the zinc oxides, which ultimately increases the rate of ORR on their surface. Thus, passivation of zinc and ORR on zinc oxides may not be mutually exclusive of each other. Oxygen may not directly participate in passivating the metal; however, it readily undergoes ORR on the surface of passive films. ORR on zinc oxides was observed to induce a polarity reversal of the passive currents, during anodic polarisation [8]. The current work supports the hypothesis [8] that it is the ORR on the zinc oxides, which results in the phenomenon of polarity reversal taking place on zinc and that may also support zinc oxide growth by a cathodically assisted process [8]. The mechanistic aspects of the impact of ORR on passive films, on passivation itself, therefore, cannot be completely ignored.

On increasing the anodic polarisation oxygen consumption by zinc is still steady in the range of 70–80 % of the bulk oxygen concentration; the exact reason for this behaviour is not clearly understood and it may be due to the fact that the ORR on zinc oxides may not be solely driven by the electrode potential of the mixed metal/semiconductor electrode but rather by some other processes taking place within the oxides or during the growth of the oxides. During depassivation, the oxygen consumption is very close to when zinc was at its initial OCP, again suggesting that some processes within the oxides may be controlling the ORR on its surface in passivating conditions.

5 Conclusion

A Pt microelectrode was used to measure the oxygen consumption on electrochemically polarised zinc. It was specifically used to qualitatively estimate the extent of oxygen consumption on zinc during anodic polarisation in the active and passive state. Zinc was anodically polarised in a pH 7 and pH 13 solution, to be subject to the active and passive state, respectively. The influence of the electrode kinetics of zinc dissolution on the oxygen diffusion towards its surface was also studied.

At similar electrode potentials (in the range from $-1.05 V_{\text{SCE}}$ to $-0.5 V_{\text{SCE}}$), the anodic currents of zinc in a pH 7 solution (in the range of 2.5–10 mA/cm^2) are significantly higher than that of zinc in a pH 13 solution (in the range of 0.01–2 mA/cm^2). The normalised oxygen current (Pt) measured at a distance of 50 μm zinc surface in pH 7 solution increases with the anodic potentials and is in the range of 0.6–0.15. The oxygen concentration measured at a distance of 50 μm from the zinc surface is, therefore, 15–60 % of the bulk oxygen concentration. This implies, correspondingly, that the oxygen consumption by zinc (due to ORR), at a distance of 50 μm from the surface is 40–85 % of the bulk oxygen concentration. In a pH 13 solution, where zinc undergoes passivation, the normalised oxygen current (Pt) is in the range of 0.2–0.3, implying the oxygen consumption by zinc due to ORR is 70–80 % of the bulk oxygen concentration. The rate of ORR on the surface of zinc passive films ($\text{ZnO}/\text{Zn}(\text{OH})_2$) is thus significant (equal or slightly higher) when compared to that on bare or actively corroding zinc. This provided supporting evidence to the model proposed in [8], wherein zinc oxides may grow by a cathodically assisted process, with the ORR favourably taking place at the oxide/solution interface, supporting the complementary anodic reaction on the metal surface. In this study, it was also demonstrated that the electrode kinetics of zinc dissolution controls the oxygen concentrations and diffusion patterns in the electrolyte.

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